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5 THOMAS V. HARRIS, a citizen of the United States of America, and resident  
6 of Benicia, County of Solano, State of California, have invented new and  
7 useful improvements in

8                   **HIGH VISCOSITY POLYALPHOLEFINS**  
9                   **PREPARED WITH IONIC LIQUID CATALYST**

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1                   **HIGH VISCOSITY POLYALPHOLEFINS**  
2                   **PREPARED WITH IONIC LIQUID CATALYST**

3                   FIELD OF THE INVENTION

4     The present invention relates to the preparation of high viscosity  
5     polyalphaolefins prepared using an ionic liquid catalyst.

6                   BACKGROUND OF THE INVENTION

7     Alphaolefins may be oligomerized to prepare synthetic lubricating oil base  
8     stocks which have desirable lubricating properties such as a low pour point  
9     and a high viscosity index (VI). However, very high viscosity polyalphaolefins,  
10    such as disclosed in U.S. Patent 4,827,064, are expensive to manufacture  
11    using conventional oligomerization processes. U.S. Patent 5,304,615 teaches  
12    the oligomerization of butene using an ionic liquid catalyst. European Patent  
13    Application 97300875.8 describes a process for oligomerizing alphaolefins,  
14    such as decene, using an ionic liquid catalyst to produce polyalphaolefins  
15    having a viscosity up to about 20 centistokes (cSt) at 100°C. Unfortunately,  
16    the process taught in this application has not been shown to be suitable for  
17    making very high viscosity material, i.e., polyalphaolefins having a viscosity  
18    above 22 cSt at 100°C.

19    Additionally, the prior art teaches the use of imidazolium, pyridinium, or  
20    phosphonium as one component in the ionic liquid in addition to aluminum  
21    halide or gallium halide. Ternary compositions with ammonium halides are  
22    described in WO 95/21872 as being useful for olefinic oligomerization.

23    Applicants have found that it is possible to readily make polyalphaolefins  
24    having very high viscosity using an ionic liquid catalyst by carrying out the  
25    oligomerization reaction in the absence of organic solvents which have  
26    hitherto been used as a diluent for the feed. Accordingly, Applicants have

1 been able to make polyalphaolefins from feeds comprised primarily of olefins,  
2 such as decene and dodecene, having viscosities in excess of 22 cSt and  
3 even in excess of 30 cSt. Polyalphaolefins made using the process of the  
4 present invention also have been shown to display excellent viscosity index  
5 (VI) values, low pour points, and low Noack volatility values.

6 As used in this disclosure, the words "comprises" or "comprising" is intended  
7 as an open-ended transition meaning the inclusion of the named elements,  
8 but not necessarily excluding other unnamed elements. The phrase "consists  
9 essentially of" or "consisting essentially of" is intended to mean the exclusion  
10 of other elements of any essential significance to the combination. The  
11 phrase "consisting of" is intended as a transition meaning the exclusion of all  
12 but the recited elements with the exception of only minor traces of impurities.

13 SUMMARY OF THE INVENTION

14 The present invention is directed to a process for producing a very high  
15 viscosity polyalphaolefin product comprising contacting a feed consisting  
16 essentially of at least one alphaolefin having from 4 to about 14 carbon atom  
17 with an effective oligomerizing amount of an acidic ionic liquid oligomerization  
18 catalyst, maintaining said feed and oligomerization catalyst under preselected  
19 oligomerization conditions for a sufficient time to oligomerize the alphaolefin to  
20 the polyalphaolefin product, and recovering the high viscosity polyalphaolefin  
21 product. As noted above, it has been found that very high viscosity products  
22 may be obtained using the process of the present invention by carrying out  
23 the oligomerization reaction in the absence of organic diluent. Using the  
24 process of the invention, polyalphaolefins having viscosities in excess of  
25 22 cSt and even in excess of 30 cSt may be readily prepared. Especially  
26 preferred in preparing the polyalphaolefin product are feeds comprising  
27 decene or dodecene.

- 1      The acidic ionic liquid oligomerization catalyst usually will be comprised of at
- 2      least two components, and in most instances it will be a binary catalyst, i.e., it
- 3      will consist of only two components. The first component is a compound
- 4      selected from the group consisting of aluminum halide, alkyl aluminum halide,
- 5      gallium halide, and alkyl gallium halide. Preferred compounds for use as the
- 6      first component of the oligomerization catalyst are an aluminum halide or an
- 7      alkyl aluminum halide, such as, for example, aluminum trichloride. The
- 8      second component is quaternary ammonium, quaternary phosphonium, or
- 9      tertiary sulfonium, such as, for example, a liquid salt selected from one or
- 10     more of hydrocarbyl substituted ammonium halides, hydrocarbyl substituted
- 11     imidazolium halide, hydrocarbyl substituted pyridinium halide, alkylene
- 12     substituted pyridinium dihalide, or hydrocarbyl substituted phosphonium
- 13     halide. Particularly preferred as the second component are alkyl substituted
- 14     ammonium halides, such as trimethylamine hydrochloride or alkyl substituted
- 15     imidizolium halides, such as 1-ethyl-3-methyl-imidazolium chloride. The mole
- 16     ratio of the two components will usually fall within the range of from about 1:1
- 17     to about 5:1 of said first component to said second component, and more
- 18     preferably the mole ratio will be in the range of from about 1:1 to about 2:1.
  
- 19     The use of a binary catalyst composition consisting essentially of
- 20     trimethylamine hydrochloride and aluminum trichloride is particularly
- 21     advantageous for carrying out the process of the present invention due to the
- 22     ease of preparation, the ready commercial availability of the components, and
- 23     the relatively low cost.
  
- 24     The amount of catalyst present to promote the oligomerization of the
- 25     alphaolefin should be not less than an effective oligomerizing amount, that is
- 26     to say, the minimum amount of the catalyst necessary to oligomerize the
- 27     alphaolefin to the desired product. This may vary to some degree depending
- 28     on the composition of the catalyst, the ratio of the two components of the
- 29     catalyst to one another, the feed, the oligomerization conditions chosen, and
- 30     the like. However, a determination of the effective catalytic amount should be

1 well within the ability of one skilled in the art with no more than routine testing  
2 necessary to establish the amount needed to carry out the invention.  
  
3 The present invention is also directed to the unique polyalphaolefin product  
4 prepared using the present invention. This product is characterized by a  
5 viscosity of not less than 22 cSt at 100°C, and more preferably will have a  
6 viscosity of at least 30 cSt at 100°C. In addition, the polyalphaolefin product  
7 will display a low pour point, preferably less than -30°C, and low volatility,  
8 preferably with a Noack number of 3 or less. Preferably, the product will have  
9 a dimer content of less than 2 weight percent.

10 DETAILED DESCRIPTION OF THE INVENTION

11 As noted above, it is essential that the oligomerization reaction be conducted  
12 in the absence of any organic diluent. In carrying out the process of the  
13 present invention, the alphaolefin feed may be added to the catalytic mixture  
14 or the catalyst may be added to the alphaolefin feed. In either case, the feed  
15 and the product formed during the oligomerization will form a separate phase  
16 from the ionic liquid which allows the two phases to be readily separated. In  
17 order to facilitate mixing of the catalyst and the feed, it is desirable to either  
18 stir the oligomerization mixture or bubble the alphaolefin feed through the  
19 ionic liquid catalyst. Following completion of the oligomerization reaction, the  
20 mixing should be halted, and the product and residual feed should be allowed  
21 to form a distinct layer apart from the catalyst phase. In previous processes,  
22 the feed and product phase usually also contained an organic diluent, such as  
23 hexane. Applicants have discovered the presence of the organic diluent of  
24 the previous processes interferes with the oligomerization reaction and  
25 prevents the formation of the desired very high viscosity polyalphaolefin  
26 product.  
  
27 The feed will consist essentially of one or more alphaolefins having from 4 to  
28 about 14 carbon atoms in the molecule, generally from about 8 to about

1    12 carbon atoms. Especially preferred are feeds containing 1-decene and  
2    1-dodecene. While the feed may consist of a mixture of different alphaolefins,  
3    it is essential that the feed not contain any organic diluent. As explained  
4    above and as further illustrated in the examples below, it has been found that  
5    the presence of an organic diluent interferes with the oligomerization reaction  
6    and prevents the formation of the desired very high viscosity polyalphaolefin  
7    product. This differs from the prior processes which included an organic  
8    diluent, such as hexane or heptane, as part of the organic phase of the  
9    reaction mixture.

10   The acidic ionic liquid oligomerization catalyst is comprised of two  
11   components which form a complex. The first component of the catalyst which  
12   will usually comprise a compound selected from the group consisting of  
13   aluminum halide, alkyl aluminum halide, gallium halide, and alkyl gallium  
14   halide. Especially preferred for the first component are aluminum halide or  
15   alkyl aluminum halide. Aluminum trichloride has been used successfully as  
16   the first component for preparing the oligomerization catalyst used in  
17   practicing the present invention.

18   The second component making up the catalyst is an ionic liquid which is  
19   primarily salt or mixture of salts which melts below room temperature. Ionic  
20   liquids may be characterized by the general formula  $Q^+ A^-$ , wherein  $Q^+$  is  
21   quaternary ammonium, quaternary phosphonium, or quaternary sulfonium,  
22   and  $A^-$  is a negatively charged ion such as  $Cl^-$ ,  $Br^-$ ,  $OCl_4^-$ ,  $NO_3^-$ ,  $BF_4^-$ ,  $BCl_4^-$ ,  
23    $PF_6^-$ ,  $SbF_6^-$ ,  $AlCl_4^-$ ,  $ArF_6^-$ ,  $TaF_6^-$ ,  $CuCl_2^-$ ,  $FeCl_3^-$ ,  $SO_3CF_3^-$ ,  $SO_3C_7H_7^-$ , and  
24   3-sulfurtrioxyphenyl. Preferred for use as the second component are those  
25   quaternary ammonium halides containing one or more alkyl moieties having  
26   from 1 to about 9 carbon atoms, such as, for example, trimethylamine  
27   hydrochloride, or hydrocarbyl substituted imidazolium halides, such as, for  
28   example, 1-ethyl-3-methyl-imidazolium chloride.

- 1 The presence of the first component should give the ionic liquid a Lewis (or  
2 Franklin) acidic character. Generally, the greater the mole ratio of the first  
3 component to the second component, the greater the acidity of the ionic liquid  
4 mixture. When aluminum trichloride and trimethylamine hydrochloride are  
5 used as the first and second components, respectively, of the acidic ionic  
6 liquid oligomerization catalyst, they preferably will be present in a mole ratio of  
7 from about 1:1 to about 2:1.
- 8 The oligomerization reaction takes place over a wide temperature range, but  
9 preferably is carried out at about ambient temperature or slightly below. The  
10 oligomerization reaction is somewhat exothermic and it may be desirable to  
11 control the reaction temperature with an aqueous quench. Preferably, the  
12 temperature of the reaction mixture will be maintained below about 50°C and  
13 most preferably will be maintained below about 30°C.
- 14 Following completion of the oligomerization reaction, the organic layer  
15 containing the alphaolefin product and residual olefin feed is separated from  
16 the ionic liquid phase. The unreacted olefin and dimers may be removed from  
17 the product by conventional means, such as by distillation, and recycled back  
18 for further conversion. Likewise, the acidic ionic liquid catalyst that remains  
19 after recovery of the organic phase may be recycled to the oligomerization  
20 zone.
- 21 Following recovery of the polyalphaolefin product, it is generally desirable to  
22 hydrogenate the unsaturated double bonds which remain in the product  
23 mixture. This is readily accomplished by conventional means well known to  
24 those skilled in the art. The hydrogenation of the unsaturated bonds is usually  
25 carried out with hydrogen in the presence of a hydrogenation catalyst such as,  
26 for example, catalyst containing nickel, palladium, platinum, cobalt or the like.
- 27 The present invention may be further illustrated by the following example  
28 which is not intended to be a limitation on the process.

PROPOSED DRAFT

1

EXAMPLE 1

2 A catalyst mixture was prepared using a 2 to 1 ratio of aluminum trichloride to  
3 trimethylamine hydrochloride. The catalyst (39.2 g) was placed in a 1 liter  
4 round bottom flask to which 401.2 g of 1-decene was added dropwise. The  
5 initial temperature of the oligomerization mixture was 0°C which was allowed  
6 to raise to 22°C. An inert atmosphere was maintained by a nitrogen sweep  
7 gas/bubbler. The reaction was allowed to proceed for 1 hour and was  
8 quenched with aqueous potassium hydroxide. The product was water  
9 washed and hydrogenated using a nickel catalyst. The residual monomer and  
10 dimer were removed by distillation. The distilled oligomer was found to  
11 display the following properties:

12	100°C Kinematic Viscosity	31.6 cSt
13	40°C Kinematic Viscosity	283 cSt
14	Viscosity Index	152
15	Pour Point	-39°C
16	Noack Volatility	1.68%

17

EXAMPLE 2

18 The general procedure was the same as in Example 1, above, except for the  
19 addition of 185 grams of heptane diluent which was mixed with 400 grams of  
20 decene. Catalyst was prepared in a 2 to 1 molar ratio of aluminum trichloride  
21 to trimethylamine hydrochloride and 40.1 grams were added to the reaction in  
22 a dropwise manner. The initial reaction temperature was -6°C. The product  
23 was water washed and hydrogenated using a nickel catalyst. The residual  
24 monomer and dimer were removed by distillation to less than 1%. The  
25 distilled oligomer was found to display the following properties:

26	100°C Kinematic Viscosity	15.0 cSt
27	40°C Kinematic Viscosity	109 cSt

RECORDED BY GENE SULLIVAN

1	Viscosity Index	143
2	Pour Point	-45°C

3 It should be noted that the kinematic viscosity of the oligomer of Example 2  
4 was significantly less at both 100°C and 40°C than that for the oligomer of  
5 Example 1. The viscosity index of the product of Example 2 was also lower.